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Author(s)	
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# Division of Synthetic Chemistry

## – Advanced Inorganic Synthesis –

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Prof  
TERANISHI, Toshiharu  
(D Eng)



Assoc Prof  
SAKAMOTO, Masanori  
(D Eng)



Assist Prof  
SATO, Ryota  
(D Sc)



Program-Specific Assist Prof  
SARUYAMA, Masaki  
(D Sc)



Program-Specific Assist Prof  
TRINH, Thang Thuy  
(Ph D)



PD  
TAKAHATA, Ryo  
(D Sc)



PD  
LIU, Ming-Han  
(Ph D)



PD  
SUZUKI, Wataru  
(Ph D)



PD  
LIAN, Zichao  
(D Sc)



PD  
KIM, Jungryang  
(D Energy Sc)



PD  
PELICANO, Christian  
(Ph D)

### Students

MATSUMOTO, Kenshi (D3)  
OKAMOTO, Yasuo (D2)  
ZHANG, Jie (D2)  
LI, Zhanzhao (D2)  
TAKEKUMA, Haruka (D1)

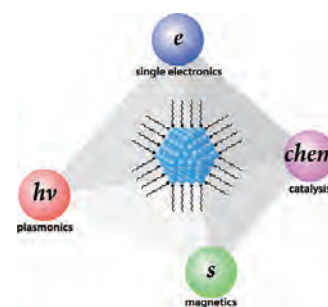
CHIGA, Yuuki (D1)  
KANEKO, Ryota (M2)  
KOSHI, Yuuki (M1)  
NAKAGAWA, Fumiko (M1)  
MANABE, Kouhei (M1)

## Scope of Research

We are focusing on the precise synthesis of inorganic nanoparticles by controlling the primary (size, shape, composition, *etc.*) and secondary (spatial arrangement) structures to tune properties such as electron confinement, carrier oscillation, spin, and catalysis. These high-quality inorganic nanoparticles are applied to both high-performance nanodevices (*e.g.*, single electron transistor, plasmon waveguide, and nanocomposite magnet) and photo-energy conversion materials (*e.g.*, overall water splitting and solar cell).

### KEYWORDS

Inorganic Nanoparticles    Single Electronics    Plasmonics  
Nanocomposite Magnet    Photocatalysts



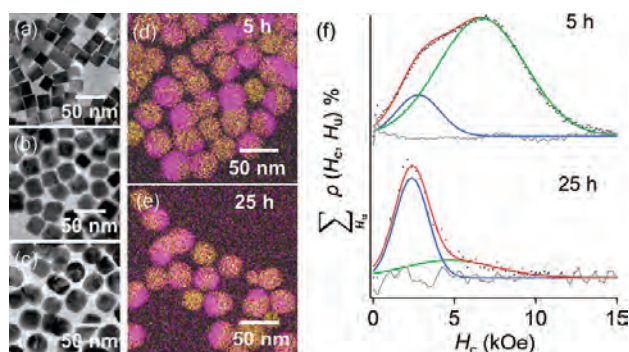
### Selected Publications

Saruyama, M.; Kim, S.; Nishino, T.; Sakamoto, M.; Haruta, M.; Kurata, H.; Akiyama, S.; Yamada, T.; Domen, K.; Teranishi, T., Phase-Segregated  $\text{NiP}_x\text{@FePyO}_z$  Core@Shell Nanoparticles: Ready-to-Use Nanocatalysts for Electro- and Photo-Catalytic Water Oxidation through *in-situ* Activation by Structural Transformation and Spontaneous Ligand Removal, *Chem. Sci.*, **9**, 4830-4836 (2018).  
Lian, Z.; Sakamoto, M.; Matsunaga, H.; Vequizo, J. J. M.; Yamakata, A.; Haruta, M.; Kurata, H.; Teranishi, T., Near Infrared Light Induced Plasmonic Hot Hole Transfer at a Nano-Heterointerface, *Nat. Commun.*, **9**, 2314 (2018).  
Eguchi, D.; Sakamoto, M.; Teranishi, T., Ligand Effect on the Catalytic Activity of Gold Clusters in the Electrochemical Hydrogen Evolution Reaction, *Chem. Sci.*, **9**, 261-265 (2018).

## Formation of Strong $L1_0$ -FePd/ $\alpha$ -Fe Nanocomposite Magnets by Visualizing Efficient Exchange Coupling

Conceptual nanocomposite magnets (NCMs) composed of exchange-coupled hard/soft magnetic phases have been expected to show excellent magnetic performance based on simultaneous high coercivity ( $H_c$ ) and high saturation magnetization ( $M_s$ ). In our previous works, however, the  $H_c$  was considerably lower than its theoretical value ( $H_a$ ), which prevented us from improving the performance of NCMs.

Here, we show that the  $H_c$  of isolated particulate  $L1_0$ -FePd/ $\alpha$ -Fe NCMs is dominated by their phase segregation into core/shell-like structures versus Janus-like structures. Using first-order reversal curve (FORC) analysis, we clearly distinguished a microscopically undetectable difference in the phase-segregation structure in the NCMs, finding both efficient and inefficient exchange coupling. The nanostructurally controlled NCMs dominated by core/shell-like structure with efficient exchange coupling showed the largest energy product ( $(BH)_{\max} = 17.5$  MGOe) in the Fe-Pd system and the highest  $H_c/H_a$  value (26.5%) among all NCM powders.

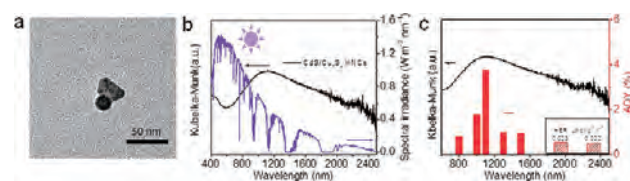


**Figure 1.** (a–c) TEM images of (a) Pd nanoparticles (NPs), (b) Pd@FeO<sub>x</sub> core@shell NPs with Fe/Pd molar ratio of 66/34, and (c)  $L1_0$ -FePd/ $\alpha$ -Fe NCMs obtained by reductive annealing of b at 540 °C for 5 h. (d, e) EDX elemental maps of  $L1_0$ -FePd/ $\alpha$ -Fe NCMs synthesized by the annealing of b at 540 °C for (d) 5 h and (e) 25 h. (f) FORCs analysis for d and e. Blue and green curves are fitting curves by a Gaussian function, corresponding to inefficient and efficient exchange coupled NCMs, respectively, red curves are the sums of green and red curves, black dots are raw data, and gray curves are difference between red curves and black dots.

## Plasmonic p–n Junction for Infrared Light to Chemical Energy Conversion

Solar light is an important energy resource for human society. The parts of the solar spectrum used for solar energy conversion, including photosynthesis and artificial photosynthesis, are limited to the ultraviolet (UV), visible, and a limited region of near infrared (NIR) light (700–1000 nm). IR light, which accounts for almost half of all solar energy, particularly IR light at wavelengths longer than 1000 nm, including shortwave IR (SWIR: 1400–3000 nm), represents a vast source of untapped energy. Developing artificial IR light-to-energy conversion systems would open up this resource for applications.

Here, we synthesized an IR-responsive plasmonic energy conversion system composed of CdS/plasmonic Cu<sub>7</sub>S<sub>4</sub> heterostructured nanocrystals (HNCs), which achieved highly efficient photocatalytic H<sub>2</sub> evolution (Figure 2a). Cu<sub>7</sub>S<sub>4</sub> NCs, which exhibit localized surface plasmon resonance (LSPR) in IR region, can be applied to harvesting solar energy in the IR region (Figure 2b). The CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs exhibited an exceedingly high apparent quantum yield (AQY) of 3.8% at 1100 nm, which exceeds the current record for photocatalytic H<sub>2</sub> evolution under IR-light irradiation (Figure 2c). Furthermore, we demonstrated that our novel HNCs can convert energy from the solar spectrum up to the longest wavelengths (*i.e.*, 2000–2500 nm). Our spectroscopic investigations using femtosecond-laser flash photolysis reveal that the high catalytic activity of our system was related to efficient hot electron injection and long-lived charge separation (> 273  $\mu$ s) at the p–n heterojunction of the CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs, which is unlike a conventional Schottky junction at the heterointerface of plasmonic metal/semiconductor NCs. The present work should encourage further development of solar fuel generation systems driven by these previously untapped solar energy resources.



**Figure 2.** (a) TEM image of CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs. (b) Solar spectrum (purple line), and diffuse reflectance spectrum of CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs. (c) Apparent quantum yield (AQY) of HER activity of CdS/Cu<sub>7</sub>S<sub>4</sub> HNCs.